



AFRL-ML-WP-TP-2007-547

OPTICAL TUNING OF THE REFLECTION OF CHOLESTERICS DOPED WITH AZOBENZENE LIQUID CRYSTALS (POSTPRINT)

Timothy J. Bunning

**Hardened Materials Branch
Survivability and Sensor Materials Division**

OCTOBER 2006

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TIMOTHY J. BUNNING, Ph.D.
Research Lead
Exploratory Development
Hardened Materials Branch

//Signature//

MARK S. FORTE, Acting Chief
Hardened Materials Branch
Survivability and Sensor Materials Division

//Signature//

TIM J. SCHUMACHER, Chief
Survivability and Sensor Materials Division

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1. REPORT DATE (DD-MM-YY)			2. REPORT TYPE		3. DATES COVERED (From - To)		
October 2006			Journal Article Postprint				
4. TITLE AND SUBTITLE			OPTICAL TUNING OF THE REFLECTION OF CHOLESTERICS DOPED WITH AZOBENZENE LIQUID CRYSTALS (POSTPRINT)		5a. CONTRACT NUMBER In-house 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER 62102F		
6. AUTHOR(S)			Dr. Uladzimir A. Hrozhik, Dr. Svetlana V. Serak, and Dr. Nelson V. Tabiryan (Beam Engineering for Advanced Measurements Corporation) Timothy J. Bunning (AFRL/MLPJ)		5d. PROJECT NUMBER 4348 5e. TASK NUMBER RG 5f. WORK UNIT NUMBER M08R1000		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)			Hardened Materials Branch (AFRL/MLPJ) Survivability and Sensor Materials Division Materials and Manufacturing Directorate Wright-Patterson Air Force Base, OH 45433-7750 Air Force Materiel Command, United States Air Force		8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-ML-WP-TP-2007-547		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			Air Force Research Laboratory Materials and Manufacturing Directorate Wright-Patterson Air Force Base, OH 45433-7750 Air Force Materiel Command United States Air Force		10. SPONSORING/MONITORING AGENCY ACRONYM(S) AFRL/MLPJ 11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S) AFRL-ML-WP-TP-2007-547		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.							
13. SUPPLEMENTARY NOTES Journal article published in Advanced Functional Materials, 2007, Vol. 17. © 2007 WILEY-VCH Verlag GmbH & Co. The U.S. Government is joint author of this work and has the right to use, modify, reproduce, release, perform, display, or disclose the work. PAO Case Number: AFRL/WS 06-2306, 27 Sep 2006. This paper contains color.							
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15. SUBJECT TERMS							
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT: SAR		18. NUMBER OF PAGES 14		
a. REPORT Unclassified		b. ABSTRACT Unclassified		c. THIS PAGE Unclassified		19a. NAME OF RESPONSIBLE PERSON (Monitor) Timothy J. Bunning 19b. TELEPHONE NUMBER (Include Area Code) N/A	

DOI: 10.1002/adfm.200600776

Optical Tuning of the Reflection of Cholesterics Doped with Azobenzene Liquid Crystals**

By *Uladzimir A. Hrozhik, Svetlana V. Serak, Nelson V. Tabiryan,* and Timothy J. Bunning**

Mixtures of cholesteric liquid crystals doped with high clearing temperature azobenzene nematic liquid crystals are shown to possess large, fast, and reversible dynamic photosensitive features. Selective wavelength shifts approaching 400 nm are reported, and depending on the host cholesteric liquid crystal, both red-shifted and blue-shifted wavelength changes can be induced. The photoinduced states of these material systems are shown to be stable for long periods of time upon removal of the radiation source, completely reversible, and dynamically fast. These phototunable features are demonstrated using both continuous wave (CW) and nanosecond laser beams. The latter is used to change the selective reflection wavelength from blue to green with a single nanosecond pulse and the ability to write information into these films using these processes are demonstrated.

1. Introduction

Photonics technologies, including optical communications, image processing, and adaptive optics, require efficient means for controlling the propagation of optical radiation. Liquid crystal (LC) electro-optical devices are at the core of many current photonic applications including beam steerers, displays, switches, and dynamic gratings. Large changes in the refractive index, low power requirements, and a robust manufacturing base have driven this commercial success. Cholesteric liquid crystals (CLCs) may combine the large optical anisotropy typical for nematic LCs with a 1D photonic bandgap structure. When aligned into the so-called planar texture, this periodic structure results from a macroscopic rotation of the director caused by molecular chirality. Such structures are distinguished by Bragg reflection of a circularly polarized light beam of the same handedness as the CLC,^[1] and when a wavelength commensurate with the visible portion of the spectrum is present, bright reflective color is observed. Both the width $\Delta\lambda$ and the position λ_B of the CLC reflection band are determined by the pitch h of the CLC, $\Delta\lambda = h(n_{||} - n_{\perp})$ and $\lambda_B = hn$, where $n_{||}$ and n_{\perp} are the local principal values of the refractive indices of the CLC and $n = (n_{||} + n_{\perp})/2$ is the average refractive index.

The ability to modulate the Bragg reflection color, both position and strength, has been a practical goal that has driven nu-

merous previous research efforts. The periodic helical structure of a CLC can be controlled with external influences, including electrical fields, temperature, and optical radiation, thus enabling dynamic Bragg gratings. The electro-optical behavior of CLCs has been explored with a number of different materials including both positive and negative dielectric materials and is discussed in numerous publications.^[2] Most of this work has centered on enabling fast, binary switching (on-off) of the reflection notch. However, because of the rather slow relaxation of electrically induced structural changes in CLCs and the formation of strongly light scattering focal conic textures in that process, optical systems based on nematic and smectic LCs are more prevalent in display- and variable color filter applications because of their higher speed of operation and simpler electro-optical characteristics.^[3,4]

The ability to dynamically change the color (wavelength tuning) has also been investigated. Complex electrode geometries, negative dielectric systems, and polymer-stabilized CLCs have shown limited success in enabling large wavelength tuning. More recently, the ability to use the radiation itself as the actuating mechanism in a variety of noncholesteric LC-based systems has been investigated by incorporating various light-responsive chromophores into the LC materials.^[5–8] Reversible light-induced changes in the molecular conformation of a photochromic guest molecules is typically used to affect local LC ordering. The ability to use this process to effectively (and reversibly) modulate the pitch of a CLC and consequently the Bragg reflection wavelength over a wide range has been a long sought-after goal; numerous papers discussing exposure to radiation have been published before^[9–20] with the first observation dated as far back as 1971.^[10] Typical shifts of the reflection notch wavelength observed to date using UV radiation are 100–150 nm.

We report here on the development of phototunable CLCs based on azobenzene nematic LCs (azo-NLCs) with extraordinarily large optical nonlinearity and photosensitivity. The de-

[*] Dr. N. V. Tabiryan, Dr. U. A. Hrozhik, Dr. S. V. Serak
Beam Engineering for Advanced Measurements Corporation
809 South Orlando Ave., Suite I, Winter Park, FL 32789 (USA)
E-mail: nelson@beamco.com

Dr. T. J. Bunning
Air Force Research Laboratory, Wright-Patterson Air Force Base
OH 45433-7707 (USA)
E-mail: timothy.bunning@wpafb.af.mil

[**] This work was supported by an AFOSR/SBIR/STTR Program and AFOSR/NL.

velopment of azo-based LC molecules that possess large mesogenic temperature ranges spanning room temperature^[21] allows for a large concentration to be mixed into commercially available CLCs. This enables large color tuning via irradiation of microwatt and even nanowatt power light beams because of photoisomerization processes of the azobenzene core. Because of the wide mesophase temperature region range and a high clearing temperature, the subsequent trans-cis isomerization of these dopants in the host CLC affects both the molecular order and the “effective” helical twisting power of the mixture without thrusting the mixture through the typical isothermal phase transition. We demonstrate here phototunable (stable and reversible) Bragg reflective materials that shift their peak wavelength ca. 400 nm when exposed to UV radiation, the highest shift reported to date. Materials that exhibit both blue and red shifts relative to the original selective wavelength using low power UV radiation are demonstrated. Once irradiated, the materials are stable for long periods of times (hours) and the reverse wavelength shift can be induced with green and red laser wavelengths. In a dramatic demonstration, a material that has had its original green selective wavelength shifted to the blue via UV irradiation is shown to respond to single nanosecond pulses of a green laser beam. These pulses induce a “reverse” red shift of the reflective notch back to the green, and patterns can be easily written using scanned beams. These CLC materials demonstrate the possibility of wide-area thin films that autonomously respond to radiation of a given wavelength, enabling new generation all-optical material systems.

2. Results and Discussion

Figure 1a shows the typical absorption spectrum of azo-NLC 1205 (BEAM Co.) in NLC 5CB (Merck). Figure 1b shows the Bragg reflection wavelength versus azo dopant concentration for a mixture of CLC 1445 (Merck) and azo-NLCs 1005 (BEAM Co.).^[21] Note that azo-NLCs are considered as the dopant in this work because of their smaller concentration in the mixture with CLC. Both, azo-NLCs 1005 and 1205 are mixtures of compounds of homologous series of 4-*n*-butyl-4'-*n*-alkoxyazobenzenes (see Experimental for structural formula). The composition of Merck’s CLC hosts 1445 and BL061 that are used in this work are not known.

Large shifts in the baseline selective-reflection wavelength from 470 to 670 nm are observed with increasing concentration. As indicated, the base CLC mixture can accommodate large amounts of the azobenzene-based LCs, in this case greater than 20 wt %. This is unlike most dye-doped LC mixtures wherein the dye acts as an impurity and only small percentages are able to be incorporated before liquid crystallinity is lost. Here, two different azo-NLCs (1005 and 1205) were dissolved in two different commercially available CLCs. In all cases, as the concentration of the trans-azo-LC increased the Bragg wavelength red-shifted, indicating that the azo-LC material was acting to reduce the pitch of the material. Table 1 shows a series of mixtures examined in this work. Note that the limiting factor for the concentration of the azo-LCs was the require-

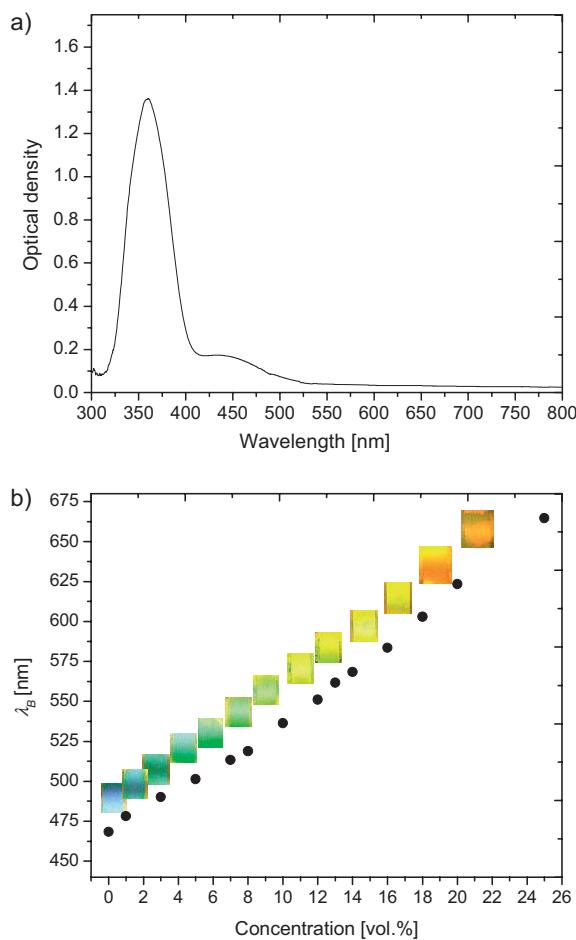


Figure 1. a) Absorption spectra of a representative azo-LC and b) Bragg reflection wavelength versus azo dopant concentration for a mixture of 1005 in 1445 along with color inserts of a 20 μ m thick CLC cell fabricated from each material.

ment to maintain the Bragg wavelength of the mixtures in the visible spectrum. At concentrations higher than 25 % the reflection band shifts into the IR region and the CLC isotropic phase transition temperature is reduced by 10–15 °C.

Examining the dependence of the Bragg wavelength on UV exposure time for several of these compositions yields a rich variety of observed effects. Figure 2a shows the dependence of the Bragg wavelength on UV exposure time for several of these compositions. Several mixtures end up with a red-shifted notch while others show a final blue shift to the notch wavelength. The time scale of the process is driven by the power and wavelength of the irradiation source. For this figure, because the wavelength of exposure (395 nm) is outside the main absorption peak of the trans isomers and because of a low power density (ca. 10 mW cm⁻²) needed to compare all mixtures, the time constants are on the order of hundreds of seconds. Irradiation time scales on the order of nanoseconds are shown to induce similar effects, as discussed below. The change in the Bragg wavelength λ_B with exposure time is an indication that either the pitch and/or the average refractive index of the CLC material is changing. The high clearing temperature of these highly

Table 1. Azo-NLC-sensitized CLC compositions and photoinduced shift in their Bragg reflection band. L : thickness of the material layer; λ_{exp} : wavelength of the radiation inducing the shift of the Bragg wavelength; $\Delta\lambda_B$: magnitude of that shift.

Azo-NLC (BEAM)	CLC (Merck)	Azo-NLC concentration in CLC [vol %]	L [μm]	λ_B [nm]	λ_{exp} [nm]	$\Delta\lambda_B$ [nm]	T_{cl} [$^{\circ}\text{C}$]
1205	1445	11	5	554	58	89	
		23	5	623	395	377	84
		23	20	625		311	84
1005	1445	0		470	0	94	
		1		476	-1	93.8	
		3		488	-3	92.8	
		5		498	-6	91.7	
		7		510	-10	90.9	
		10		536	-17	89.6	
		12	3	552	-16	89	
		13		557	409	-11	88.4
		14		568		-8	87.5
		16		589		-6	86.7
1005	BL061	18		610		4	85.6
		20		632		43	85
		23		655		78	83.9
		25		676		134	83
		0		468	0	86	
1005	BL061	3		501		-13	84.5
		7		535		-29	82
		9		552	409	-38	81
		11		570		-46	79
		25		683		-31	71

doped systems enables the mixture to retain its mesogenicity under prolonged exposure to UV and blue radiation. For most dye-doped systems wherein one uses radiation to enable the isothermal nematic-isotropic transition, mixtures that have clearing temperatures close to room temperature are the most effective. Here, by utilizing mixtures that have a high clearing temperature, large amounts of cis monomers can be achieved in the irradiated samples without causing the typical isothermal phase transition to occur. The temporal stability of the color obtained once irradiation is turned off is on the order of hours as shown in Figure 2b. Thus, any color can be “dialed-in” by simply controlling the illumination time. The color change can be reversed by illumination with a green or red laser wherein the reverse cis-trans reaction occurs, again on fast time scales as demonstrated later.

Figure 3 shows several visual representations of what happens when such mixtures are irradiated. The green outer part in Figure 3a is the original color of the CLC. A selective reflection wavelength in the blue (and thus a final blue shift) is obtained upon illumination with radiation of 409 nm wavelength and 3.2 mW power (68 mW cm^{-2} power density). The green central spot is the restored color of the CLC that occurred upon exposure to an Ar^+ laser beam of 488 nm of 0.37 mW power (108 mW cm^{-2}). The dynamics of such color shifts are shown in Figure 3b where the shaded areas mark the time intervals where the violet laser is exposing the original. The y-axes are the normalized reflection and transmission coefficient measured using the Ar^+ beam as a probe. Compared to Figure 2a,

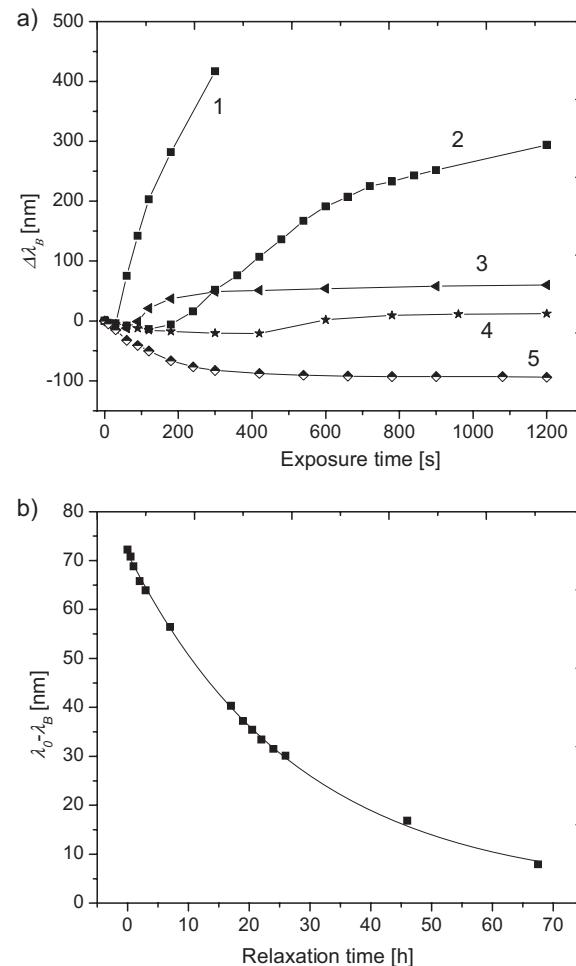


Figure 2. a) Shift of the Bragg wavelength as a function of UV exposure time for several azo-NLC/CLC compositions ($\lambda_{\text{exp}}=395 \text{ nm}$, $I=10 \text{ mW cm}^{-2}$): 1205(11%)/1445, $L=5 \mu\text{m}$ (1); 1205(23%)/1445, $L=5 \mu\text{m}$ (2); 1205(23%)/1445, $L=20 \mu\text{m}$ (3); 1005(11%)/1445, $L=30 \mu\text{m}$ (4); 1005(18%)/BL061, $L=20 \mu\text{m}$ (5). b) Dynamics of the Bragg reflection wavelength resulting from cis-isomer relaxation for UV-pre-exposed material 1005(7%)/BL061. A CLC cell, 6 μm thick, was exposed to UV radiation ($\lambda_{\text{exp}}=365 \text{ nm}$, $I=10 \text{ mW cm}^{-2}$) for 1 min and then the relaxation back to the original reflective wavelength was monitored. The time constant of the Bragg reflection band restoration is approximately 28 h.

much faster time constants are realized and the effect of power density on both the relaxation and the restoration in this example is shown in Figure 3c. This speed can also be effected greatly by changing the illumination wavelength to 365 nm as shown in Figure 3d. Because absorption and thus the production of cis isomers is so much more effective at this wavelength, faster switching speeds can also be realized. The insets show the color of 6 μm thin films of the same sample, one after illumination of 532 nm and the other after exposure to 365 nm radiation. The decrease of the response time with increasing power density of the UV radiation is demonstrated in Figure 4.

Figure 5 shows the photoinduced shift in the reflection spectra of CLC 1445 doped by 23 vol % azo-NLC 1205 [1205(23%)/1445] wherein the largest changes of the Bragg wavelength is observed. Violet radiation of an light-emitting

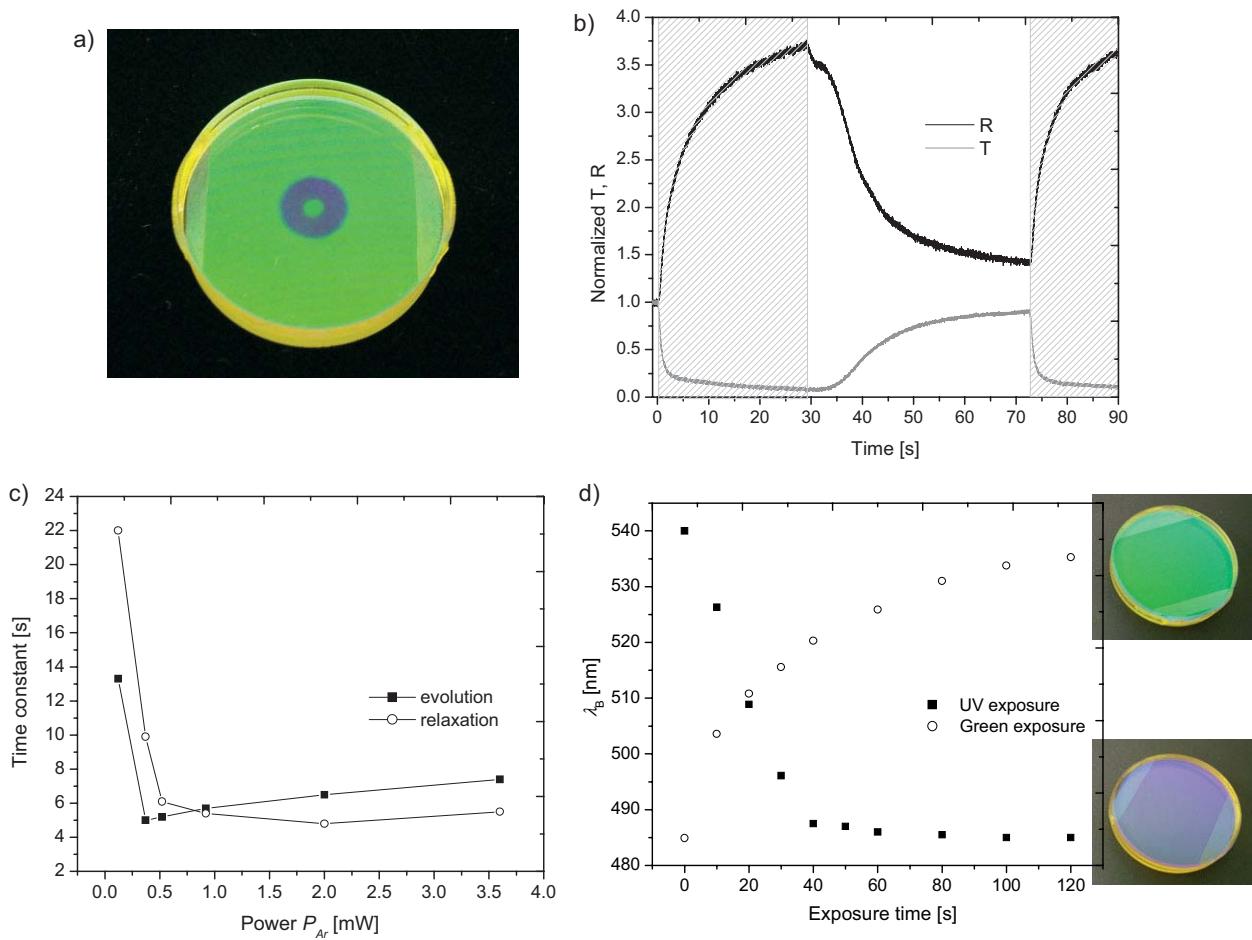


Figure 3. a) Photo of CLC cell 1005(7%)/BL061 that has been uniformly illuminated by a 409 nm laser beam causing a blue shift of the original color from green to blue. The center spot was subsequently irradiated with an Ar^+ laser at 488 nm causing the relaxation of this area back to green. b) Dynamics of both processes as monitored using the Ar^+ laser at 488 nm. c) The effect of power density on the time constant for both processes. d) The spectral shift of this material as a function of time for irradiation at 365 nm and 532 nm (10 mW cm^{-2}).

diode (LED) matrix ($\lambda = 395 \text{ nm}$, $I = 10 \text{ mW cm}^{-2}$) tuned the position of the reflection band of this material from 625 nm to 1000 nm, almost a 400 nm shift in the peak wavelength. The effect of azo-NLC concentration can be seen in Figure 5b where the magnitude of $\Delta\lambda_B$ is plotted for 3 μm thick layers of 1005/1445 mixtures as a function of their exposure time to a violet laser beam ($\lambda = 409 \text{ nm}$): the higher the concentration of azo-NLC, the larger $\Delta\lambda_B$ and the sensitivity (steeper slope). At relatively large concentration values, $\Delta\lambda_B$ is a nonlinear function of azo-NLC concentration, which is expected given the proximity of the photoinduced isothermal phase transition region, as indicated in Figure 5c. For all samples, the sign of the wavelength shift is first negative (blue shift) and then starts back towards the positive. Whether the final wavelength achieved is net blue- or red-shifted relative to the starting wavelength is highly dependent on the initial CLC mixture, as shown in Table 1. For the azo-NLC 1005 in CLC 1445, as concentration is increased, the final wavelength shift starts out at -1 nm , reaches a maximum blue shift of -11 nm at 13 %, and then ends up at $+134 \text{ nm}$ at 25 %. The same azo-LC material doped in BL061 starts with a -13 nm shift for 3 wt %, increases to

-46 nm at 11 wt %, and then comes back to a value of -31 nm for 25 wt %.

The mixtures we have studied are in the liquid crystalline phase at room temperature and are characterized by rather high clearing temperatures. The phase transition temperature from a CLC to an isotropic phase measured with $0.1 \text{ }^\circ\text{C}$ accuracy for all mixtures is shown in Table 1. The effect of temperature on the Bragg wavelength is small compared to the effect of photoisomerization as it is seen in Figure 5d for two azo-NLC-doped CLC mixtures. The maximum thermally induced shift of the Bragg wavelength is only $(\Delta\lambda_B)_T = 30 \text{ nm}$ for the red-shifting mixture of azo-NLC 1005 (25 wt %) in CLC 1445 as opposed to $(\Delta\lambda_B)_{Ph} = 134 \text{ nm}$ for phototuning. For the blue-shifting mixture of azo-NLC 1005 (25 wt %) in CLC BL061, we measured $(\Delta\lambda_B)_T = -3 \text{ nm}$, which is also nearly an order of magnitude smaller than the photoinduced shift equal to $(\Delta\lambda_B)_{Ph} = -31 \text{ nm}$. Practically no thermally induced changes in the Bragg wavelength were registered for both materials up to $40 \text{ }^\circ\text{C}$, as evident from Figure 5d. Since phototunable properties of these materials were studied at room temperature using low-power laser beams, we can conclude that the temperature

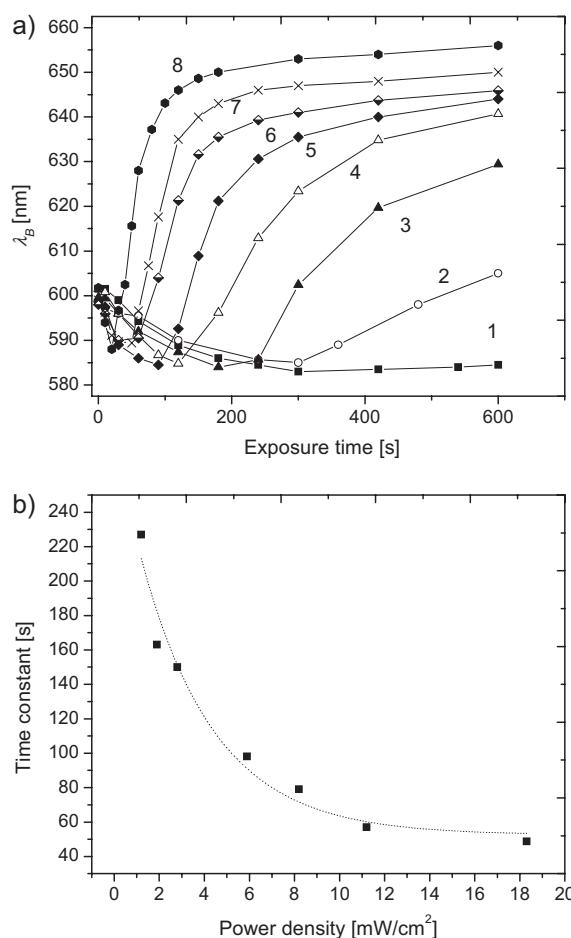


Figure 4. a) Bragg reflection wavelength versus exposure time for the material 1005(18%)/1445 ($\lambda_{exp}=395$ nm, $I=10$ mW cm⁻²): 1 mW cm⁻² (1); 1.2 mW cm⁻² (2); 1.9 mW cm⁻² (3); 2.8 mW cm⁻² (4); 5.9 mW cm⁻² (5); 8.2 mW cm⁻² (6), 11.2 mW cm⁻² (7); 18.3 mW cm⁻² (8). b) Time constant as a function of power density.

of the materials does not change substantially and does not affect the photoinduced processes.

The wavelength of reflection is dictated by two parameters, the average index of refraction, n , and the pitch of the material, h . The average refractive index n of a CLC depends strongly on both the concentration of cis isomers and the strong influence of these isomers on the order parameter. The average refractive index n can be shown as $n=(n_{\parallel}+n_{\perp})/2=n_{\perp}+(n_{\parallel}-n_{\perp})/2$. The optical anisotropy of the material $n_{\parallel}-n_{\perp}$ decreases with decreasing order parameter which indicates that the effect of radiative trans-cis photoisomerization is to lower the overall average refractive index resulting in a finite blue shift of the Bragg wavelength in all materials. The upper limit of the change of the average refractive index is set by phase transformation into an isotropic state

$$\Delta n = \frac{n_{\parallel} + n_{\perp}}{2} - \frac{n_{\parallel} + 2n_{\perp}}{3} = \frac{n_{\parallel} - n_{\perp}}{6}$$

Although relatively small at $\Delta n \approx 0.03$ (for a typical value of the optical anisotropy of the material $n_{\parallel}-n_{\perp}=0.2$), as demon-

strated, this change can result in a change of the Bragg wavelength by as much as 20 nm. Thus, blue shifts of this magnitude are expected for highly doped samples wherein one lies close to the isothermal phase transition point.

The effect of changing the CLC pitch becomes prevalent, $n\Delta h > h\Delta n$, at longer exposure times due to, particularly, the slowness of director reorientation processes. The resulting shift in the Bragg wavelength, $\Delta\lambda_B = h\Delta n + n\Delta h$, therefore becomes red for mixtures with $\Delta h > 0$, or enhanced further in the blue for mixtures with $\Delta h < 0$. The magnitude of the CLC pitch h is determined by the concentration of the chiral molecules and is related to the helical twisting power of the molecular system. To a first approximation, any nonchiral molecule including both the trans and cis azo molecule will act as a dopant, reducing the helical twisting power of the system, thus red-shifting the wavelength as shown in Figure 1b. If the cis molecule is more effective in “diluting” the chiral mesogenic order than the trans molecule, a further red-shift is expected as a result of trans-cis photoisomerization. If the cis molecule does not affect the internal structure as much (i.e., a shallower slope in Fig. 1b), then one would expect a blue-shift of the wavelength relative to the all-trans case. Any change in the pitch upon irradiation, and thus, formation of cis molecules other than that expected by the small change in refractive index, indicates that the influence of the cis molecules as a dopant is different than the influence of the trans molecules. Data shown in Figure 6 confirms this behavior as the Bragg wavelength of CLC BL061 as a function of concentration of trans- and cis isomers of azo-NLC 1005 is shown. In order to control the quantity of the azo-NLC for doping the CLC, a measured quantity of azo-NLC 1005 was spread on a glass and was subjected to UV radiation ($\lambda_{exp}=365$ nm, $I=10$ mW cm⁻²) for 8 h. The slope of the cis isomer is shallower in this case indicating a weaker effect on the pitch. Table 1 confirms that compared to the case of all-trans isomers, this weaker influence on the pitch results in a net blue-shift in wavelength.

The specific molecular details of the individual systems which dictate either a net blue-shift (effective increase in the helical twisting power) or a red-shift (effective decrease in the helical twisting power) is still unclear. Further experiments are underway to determine the large difference in behavior for the cis- and trans-molecules when doped into base CLC mixtures. Finite solubility places an upper limit on the change in the CLC pitch that can be obtained by increasing the dopant concentration in a CLC.

Photoinduced isomerization of azo molecules takes place within 10^{-9} s, as has been documented.^[22] Therefore, one could expect that CLCs photosensitized by azo-LC dopants should be responsive to short laser pulses because of the high energy density. A CLC 1005(7%)/BL061 mixture in a 6 μ m thick cell whose original Bragg wavelength was 535 nm was first exposed to UV radiation that shifted its reflection band towards violet wavelengths, as shown previously in Figure 3d. Single-shot laser pulses of nanosecond duration (532 nm) focused by a lens of 100 mm focal length proved capable of restoring (cis-trans isomerization) the green reflection state of the CLC. The sample was tested in different positions in the focal region of the

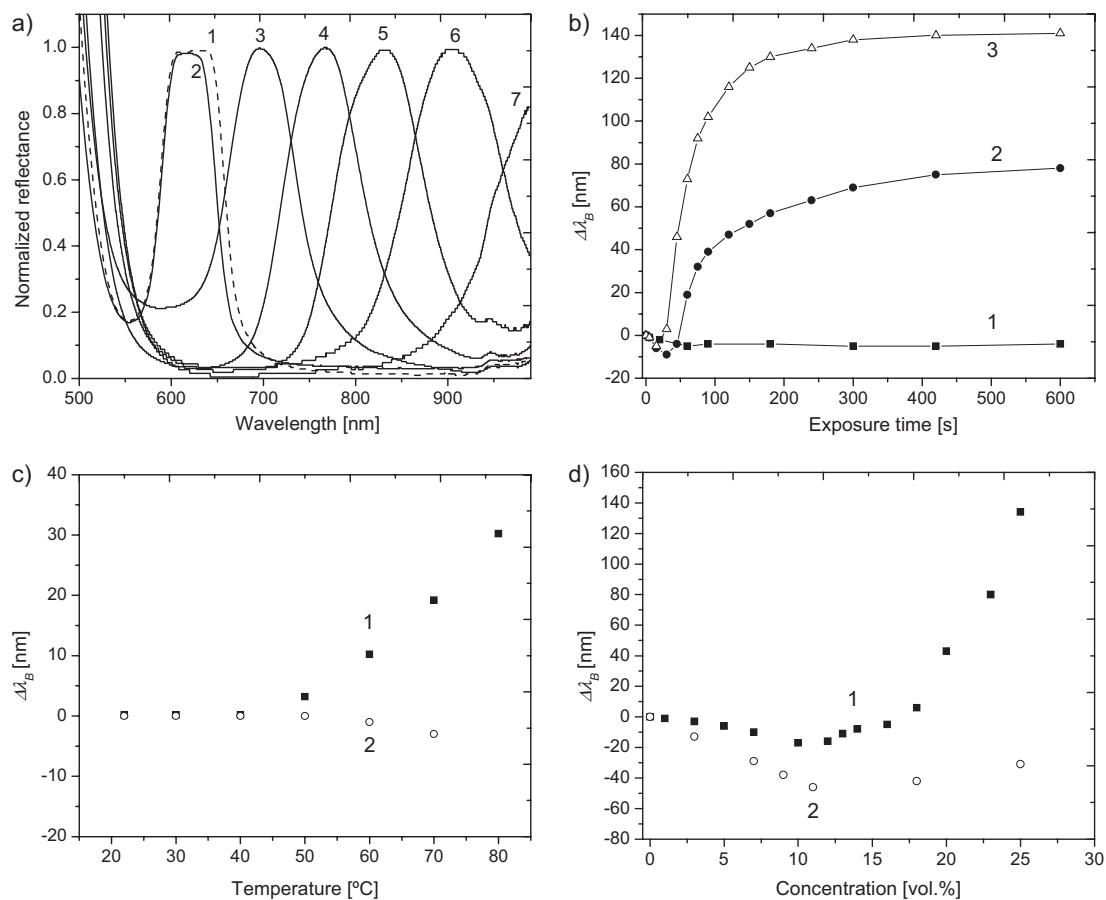


Figure 5. Photoinduced shift in the relative Bragg reflection band of 5 μm thick CLC 1205(23 %)/1445 upon illumination by a violet LED ($\lambda_{\text{exp}} = 395 \text{ nm}$, $I = 10 \text{ mW cm}^{-2}$): a) Absorption spectrum. The corresponding exposure times are: 0 s (1); 30 s (2); 60 s (3); 90 s (4); 120 s (5); 180 s (6); 300 s (7). b) Shift of the Bragg wavelength as a function of exposure time for different concentration of azo-NLC 1005 in CLC 1445: 1 vol % (1); 23 vol % (2); 25 vol % (3). The thickness of the material samples in these tests is 3 μm , and they are exposed to a violet laser beam ($\lambda_{\text{exp}} = 409 \text{ nm}$). c) Thermally induced shift of Bragg wavelength for red-shifting CLC composition 1005(25 %)/1445 (1) and blue-shifting CLC composition 1005(25 %)/BL061 (2). d) Reflection band shift versus azo-NLC concentration for two compositions: 1005/1445 (1) and 1005/BL061 (2). ($\lambda_{\text{exp}} = 409 \text{ nm}$, $I = 10 \text{ mW cm}^{-2}$, exposure time: 60 s.).

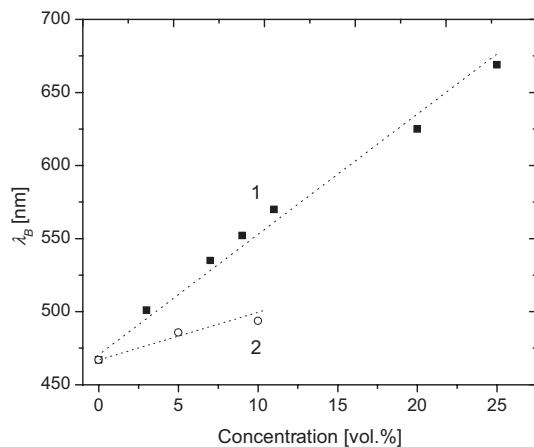


Figure 6. Bragg reflection wavelength for the composition 1005/BL061 as a function of concentration of azo-NLC 1005 in trans form (1) and in cis form (2) to the CLC BL061. The cis form of azo-LC 1005 was obtained by exposing the material to UV radiation ($\lambda_{\text{exp}} = 365 \text{ nm}$) for 8 h.

lens for beam-diameter values varying in the range of 60–200 μm . The green spots seen in Figure 7 were recorded by single laser pulses of nanosecond duration and 1–1.6 mJ energy and resulted from the photoinduced shift of the CLC bandgap

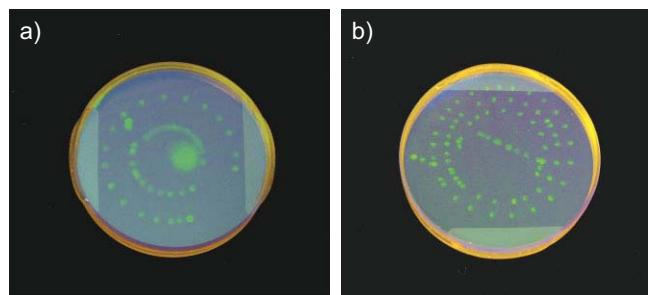


Figure 7. Examples of restoration of the green reflection wavelength by single laser pulses of nanosecond duration: a) and b) correspond to different focusing conditions.

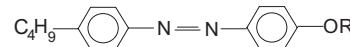
from blue to green wavelengths. Although the detailed dynamics of the blue-to-green shift have not been studied yet, this transformation occurs on the order of microseconds. The spots, once formed, are stable on the order of an hour with the green spots relaxing back to blue as a result of diffusive processes. Over extended periods of time, the dark *cis*–*trans* relaxation will eventually convert the entire film to its energetically favorable green reflective state. The exposure energy density for the pulsed laser evaluated from the pulse energy (1.6 mJ) and beam diameter (0.6 mm) is 560 mJ cm^{-2} . This is close to the exposure energy density for continuous wave (CW) radiation producing a comparable shift in the Bragg wavelength (10 mW cm^{-2} @ 40 s).

Figure 8 shows a set of lines recorded in photosensitized CLC cells by scanning it at the speed of $615 \mu\text{m s}^{-1}$ across a laser beam of nanosecond pulses at 10 Hz frequency. Under these conditions, the travel distance of the cell from pulse to

sensitive features in thin films formed using these mixtures. Large shifts in the reflection wavelength with low laser power were demonstrated. These photosensitive features were demonstrated using both CW and nanosecond laser beams as was the ability to utilize these features to write, reversibly, information into the films. These photosensitive CLC materials will allow the development of spectral as well as spatial filters with resolution and response times well beyond capabilities of current electro-optical systems. Their design and manufacturing simplicity combined with their low cost are important preconditions for future applications and development of all-optical systems with customized properties. This work is enabled by the development of azo-based nematic liquid crystals that can be dissolved in CLCs in large concentrations without destroying the CLC structure, enabling large photosensitivity.

4. Experimental

Two types of CLCs were used as hosts for azo-NLC in the present study: BL061 and MDA-00-1445. These materials are available from Merck Ltd., exhibit Bragg reflection wavelengths of 467 and 468 nm and clearing temperatures of 86 and 94 °C. The two types of azo-NLCs used for photosensitizing the host CLCs are products of BEAM Engineering for Advanced Measurements Co. (BEAM Co.). The materials 1005 and 1205 are two and three component compositions based on the series of 4-*n*-alkyl-4'-*n*-alkoxyazobenzenes



where R = CH₃ (4-*n*-butyl-4'-methoxyazobenzene), R = C₂H₅ (4-*n*-butyl-4'-ethoxyazobenzene), and R = C₅H₁₁ (4-*n*-butyl-4'-pentyloxyazobenzene). They are distinguished by a wide temperature range of the nematic phase including room temperature (12.5 N 49 I and 8 N 59 I) and birefringence values of 0.18 and 0.21. The optical anisotropy of the materials Δn is measured at a wavelength of 633 nm.

Photosensitivity of these materials can be characterized by the so-called incubation energy E_{inc} which describes the initial stage of photo-induced nematic–isotropic phase transition [24]. Accumulation of *cis* isomers at this stage results in changing of the order parameter of the azo-NLC without starting the critical process of phase transition. At this stage, the transmission of the material does not change even though the phase of a laser beam changes according to the effect of the order parameter on the refractive index of the material. The transmission of the material starts decreasing upon further accumulation of *cis* isomers due to generation of microdomains of isotropic phase. The energy required for completion of the phase transition and obtaining a homogeneous isotropic state E_{iso} is typically 2–3 times larger than the incubation energy. These parameters are equal to $E_{\text{inc}}=0.073$ and $E_{\text{iso}}=0.13 \text{ J cm}^{-2}$ for azo-NLC 1005, and $E_{\text{inc}}=0.39$ and $E_{\text{iso}}=0.73 \text{ J cm}^{-2}$ for azo-NLC 1205, correspondingly. The measurements were performed for 10 μm thick samples exposed to $I_{\text{inp}}=6.2 \cdot 10^{-3} \text{ W cm}^{-2}$ power density of a laser beam of 409 nm wavelength polarized parallel to the planar orientation of the azo-NLCs.

Table 1 summarizes most material compositions tested in this work and the magnitude of the photoinduced shift in their Bragg wavelength.

Received: August 24, 2006

Revised: October 31, 2006

Published online: June 29, 2007

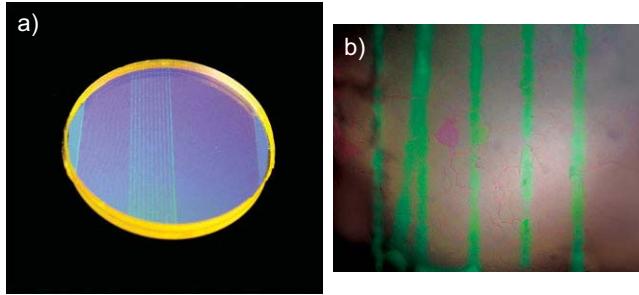


Figure 8. a) Photo of a CLC cell with a set of lines recorded in a $L=6 \mu\text{m}$ thick layer of the CLC 1005(7%)/BL061 by scanning it at the speed of $615 \mu\text{m s}^{-1}$ across a laser beam of nanosecond pulses at 10 Hz frequency. The beam is focused by a lens with a focal length $F=100 \text{ mm}$. Pulse energy: $55 \mu\text{J}$; distance between the lines: 0.5 mm ; line thickness: $160 \mu\text{m}$. b) Photo taken under a microscope.

pulse is about $60 \mu\text{m}$, which is smaller than the radius of the beam on the sample (note again that the sample is out of the focus), hence the spots restored to their green reflection state overlap, forming lines along the scan direction. The higher the pulse energy, the thicker the exposed lines.

Thus, single nanosecond pulses are capable of shifting the Bragg reflection band of the CLC from violet to green wavelengths. It will be very interesting in the future to study the dynamics of the restoration process and its dependence on pulse energy. *Trans*–*cis* photoisomerization results in a change of the average refractive index due to a reduced order parameter as well as the difference in molecular polarizability between *cis*-and *trans* isomers.^[23] The latter effect can affect the position of the Bragg reflection band of CLCs within the pulse duration time.

3. Conclusion

In the present work, we have shown that doping CLCs with azo-NLCs possessing large mesophase ranges is a promising approach to impart large, fast, and reversible dynamic, photo-

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